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Intramolecular C-H...N and intermolecular N-H...N interactions in 2-amino-4-phenyl-1,3-thiazole

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Abstract . The crystal structure of 2-amino-4-phenyl-1, 3-thiazole derivative has been determined by X ray diffraction methods with an aim of describing intra- and intermolecular interactions in thiazoles The title compound crystallizes in tetragonal space group $P4_1$ and its structure has been refined upto the reliability index of 5%. There occurs N-H .N bond at a distance of 2 19 and 3 01Å, respectivley and it appears to be formed by symmetry-related amino atom and nitrogen atom of the parental thiazole ring The crystal cohesion is pronounced, may be due to an intramolecular phenyl-thiazole C-H...N interaction.

Keywords Structure analysis, crystal data, packing interactions, symmetry code

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1. Introduction

The hypoglycaemic [1], carcinostatic [2], carbonic anhydrase [3,4] and tuberculostatic [5] properties as exhibited by thiazole derivatives have made them important chemotherapeutic agents. 2-aminothiazoles are also known to inhibit the corrosion of mild steels as well as copper alloys and is used as a brightner in electroplating industry [6]. The title compound is known to have been used for the preparation of industrial colouring materials [7]

2. Experimental

2.1 *Synthesis :*

To the solution of thiourea 7.6g (0.1 mole) in water (20ml) in a three-necked flask equipped with a sealed stirrer, a reflux condenser and dropping funnel to which 7.7g (0.1 mole) of chloroacetophenone have been added over the period of thirty minutes and refluxed further for a period of two hours and then cooled. The separated solid extracted with ether (25ml) and dried with anhydrous Na_2SO_4. Removal of ether on rotatory evaporation yielded transparent crystals of the title compound

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2.2 *Crystal data :*

Three-dimensional intensity data of a transparent plate like single crystal (0.3 × 0.1 × 0.1 mm) of 2-amino-4-phenyl-1, 3-thiazole ($C_9H_8N_2S$) (m.p. 424K) were collected on an Enraf-Nonius CAD-4 diffractometer using MoKα radiation (λ = 0.71073 Å). The title compound crystallizes in tetragonal space group $P4_1$ with unit cell dimensions : a = 12.124(3), b = 12.124(2), c = 5.759(3) Å and the number of molecules per unit cell (Z) is 4. The calculated density and unit cell volume are 1.383 Mg/m^3 and 846.5(5)Å^3, respectively. $\omega/2\theta$ scan mode was employed for data collecion with θ-ranging from 2.38 to 24.94°. The cell parameters were refined from accurately determined 25 reflections in the θ-range $9.73 \le \theta \le 11.32^0$. A total of 886 reflections were measured out of which 808 were found unique $(0 \le h \le 14, 0 \le k \le 14, 0 \le l \le 6)$ and 760 as observed $[F_0 > 4\sigma(F_0)]$. Two standard reflections ($1\,\bar{5}\,\bar{2}$ and $1\,\bar{5}\,\bar{3}$) measured every hundred reflections, showed no significant variation in the intensity data. The reflection data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied.

2.3 *Structure analysis :*

The structure has been determined by direct methods using SHELXS97 program [9]. All non-hydrogen atoms of the molecule

were located from the *E*-map. Full-matrix least-squares refinement of the structure has been carried out by using SHELXL97 program [10]. The positional and thermal parameters of non-hydrogen atoms were refined isotropically with residual index, $R = 0.133$. Further refinement with anisotropic thermal parameters and fixing of hydrogen atoms stereochemically resulted in the final value of the reliability index, $R = 0.050$, with weighted $R(F^2) = 0.149$. The maximum and minimum value for the residual electron density is 0.30 and -0.24 eÅ^{-3}, respectively. The maximum shift $[(\Delta/\sigma)_{max}]$ is 0.06Å and Goodness-of-fit on F^2 is 1.109. Atomic scattering factors have been taken from International Tables for Crystallography (1992, Vol. C Tables 4.2.6.8 and 6.1.1.4). The final atomic positions and equivalent isotropic displacement parameters for all the non-hydrogen atoms are listed in Table1.

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å^2) (with e s.d 's in parentheses) for the non-hydrogen atoms

Atom				U_{eq}
S1	0 7324(1)	0 3828(1)	0 0877(3)	0 064(1)
N2	0.6348(4)	0.3786(4)	0.5052(11)	0.071(2)
N3	0.7724(3)	0 5123(3)	0 4328(10)	0 053(1)
C2	0.7096(4)	0 4289(4)	0.3691(12)	0 053(2)
C4	0.8412(4)	0 5431(4)	0.2524(11)	0.046(1)
C5	0.8318(4)	0 4830(4)	0.0589(12)	0.056(2)
C6	0.9205(3)	0.6359(4)	0.2888(10)	0 046(1)
C7	0.9176(4)	0 6984(4)	0 4884(13)	0.056(2)
C8	0 9923(5)	0.7848(5)	0.5159(14)	0.065(2)
C9	1.0698(5)	0 8077(5)	0 3485(16)	0 068(2)
C10	1 0730(4)	0 7450(5)	0 1482(15)	0.067(2)
C11	0 9987(4)	0.6589(4)	0.1178(12)	0.057(2)

$$^{*}U_{eq} = (1/3)\sum_{i}\sum_{j} U_{ij} a_i {}^{*}a_j {}^{*}(a_i . a_j)$$

A general view of the molecule drawn at 50% probability level with atomic numbering scheme is presented in Figure 1 [11]. The geometrical calculations were performed by using the PARST program [12].

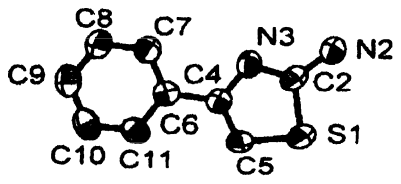

Figure 1. ORTEP view of the molecule drawn at 50% probability level with atomic numbering scheme.

3. Results and discussion

3.1 Bond lengths and bond angles :

The bond distances and bond angles are presented in Table 2. Bond lengths within the thiazole ring have been compared with the corresponding values from some related structures [13-15]. The mean bond length [C(sp3)–N] = 1.364(8) is quite close to that of some chemically similar looking compounds [16, 17]. The

Table 2. Bond distances (Å) and bond angles (°) for non-hydrogen atoms (e.s.d 's are given in parentheses).

S1–C2	1.736(7)	C6–C7	1 377(9)
C5–S1	1.719(5)	C6–C11	1 395(8)
N2–C2	1.345(8)	C7–C8	1 394(8)
N3–C2	1.318(6)	C8–C9	1 374(10)
N3–C4	1.384(8)	C9–C10	1 382(12)
C4–C5	1.336(9)	C10–C11	1 390(7)
C4–C6	1.495(7)		
C2–S1–C5	88 5(3)	C4–C6–C11	119 2(4)
C2-N3–C4	110.3(4)	C4–C6–C7	121 0(4)
N2–C2–N3	125 1(5)	C7–C6–C11	119 8(5)
S1–C2–N3	114.5(4)	C6–C7–C8	119 5(5)
S1–C2–N2	120 4(5)	C7–C8–C9	121 1(6)
N3–C4–C6	119 0(4)	C8–C9–C10	119 6(7)
N3–C4–C5	115 3(5)	C9-C10–C11	120 0(6)
C5–C4–C6	125 6(5)	C6–C11–C10	120 1(4)
S1–C5–C4	111.4(4)		

distances of interest in the molecule are S1-C2 [1.736(7)Å] and C5-S1 [1.719(5) Å], as these distances are comparable with the corresponding values of some analogous structures presented in Table 3.

Table 3. A comparison of S-C and C-S bond lengths of some thiazole moieties.

Molecule and reference	S(1)–C(2)	C(5)–S(1)
Thiazole derivative–I [Ref. 6]	1.763	1 739
Thiazole derivative–II [Ref. 13]	1 763	1 739
Thiazole derivative–III [Ref. 14]	1.776	1 813
Thiazole derivative–IV [Ref. 15]	1.671	1 712
Thiazole derivative–V [Ref. 22]	1.700	1 710
Thiazole derivative–VI [Ref. 23]	1.749	1 757
Thiazole derivative–VII [Ref. 24]	1 742	1 720
Thiazole derivative–VIII [Ref. 25]	1.726	1 864
Thiazole derivative–IX [Ref. 26]	1.777	1 765
Thiazole derivative–X [Ref. 27]	1.771	1 839
Thiazole derivative–XI [Present work]	1.736	1 719

The bond angles agree well with some analogous thiazol derivatives [13-15]. The angle endocyclic bond angle *i.e.* C5-S1

C2 [88.5(3)°] is found to have significantly less value as compared to the remaining bonds of the ring [16]. The endocyclic bond angles fall in the range 88.5(3) to 115.3(5)° [average value being 108(3)°] for the azole ring. Both the thiazole and phenyl rings adopt planar conformations with average value of torsion angles 0.7(6) and 0.6(9)°, respectively. There is a dihedral angle of 6.5(2)° between the two rings. The amino group substituted at position C2 is deviated by –0.022(5)Å from the mean plane of thiazole ring.

Molecular packing and hydrogen bonding :

In the tetragonal $P4_1$ space group, the molecules of 2-amino-4-phenyl-1, 3-thiazole are linked by paired C-H...N and N-H...N hydrogen bonds into $C_1^2(4)$ motif (where *C*, refers to chain or catemer; 2, no. of donors; 1, no. of acceptors; 4, no. of atoms involved) [18]. In both the C-H...N and N-H...N bonds, the hydrogen donor atoms are C7 and N2 while N3 is the only acceptor atom. The molecules are linked through a chain of N-H...N hydrogen bonds. The N(amino)-H bond in the molecule at (*x*, *y*, *z*) form a hydrogen bond (Table 4) with the N(thiazole) atom of the molecule at (–*x* + 1, *y*, *z*–1/4), making the molecules looking like a cavity-shaped structure, typical of host-guest nature

Table 4. Geometry of intra- and intermolecular interactions (e.s.d.'s are given in parentheses)

D-H...A	H...A(Å)	D...A(Å)	D-H...A(°)
C7 - H7...N3	2.559(7)	2.880(6)	100.6(5)
N2 - H2B...N3$^{(i)}$	2.196(7)	3.001(7)	155.7(6)

Symmetry code (i) –*x* + 1, +*y*, +*z* –1/4

The packing diagram as projected in Figure 2 illustrates the hydrogen bond pairing of amino groups at crystallographic sites along the '*a*' and '*b*' edges of the chosen cell. The structure is stabilized by an intramolecular C (sp^3)–H....N interaction and an intermolecular N (amino)–H...N(thiazole) interaction. There is an intermolecular N–H...N close contact of 2.19Åwith the hydrogen (H2B) of the amino group. Using complied data for a large number of N–H..N contacts, Steiner and Desiraju [19] find significant statistical directionality even as far out as 3.0Å, and conclude that these are legitimately viewed as 'weak' hydrogen bonds, with a greater contribution to packing forces than simple van der Waals attractions. These packing interactions which are depicted in Figure 2, could be termed as *Steering* or *tugboat* [20] and these are responsible for generating a three-dimensional network [21].

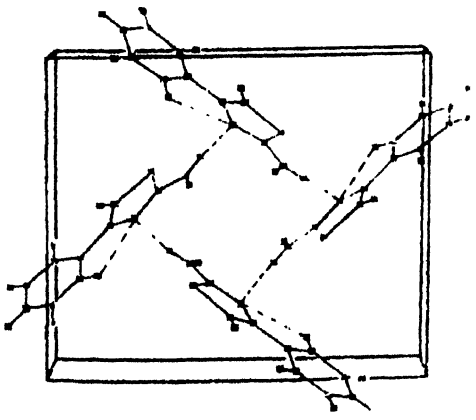

Figure 2. Packing diagram viewed down *c*-axis

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